A Path Forward to Advanced Nuclear Fuels: Spectroscopic Calorimetry of Nuclear Fuel Materials

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A Path Forward to Advanced Nuclear Fuels:
Spectroscopic Calorimetry of Nuclear Fuel Materials

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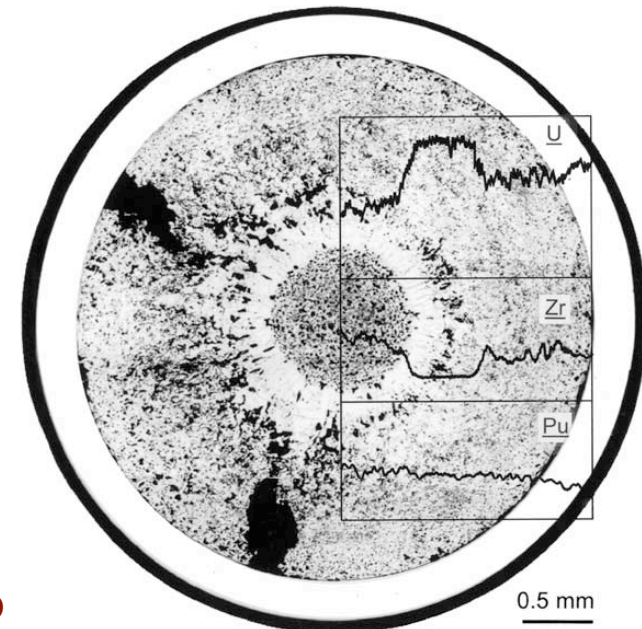**In association with Uppsala University, Sweden**

A Path Forward to Advanced Nuclear Fuels: Spectroscopic Calorimetry of Nuclear Fuel Materials

- **Goal: Relieve the shortage of thermodynamic and kinetic information concerning the stability of nuclear fuel alloys.**

- **Challenge: Past studies of the ternary nuclear fuel UPuZr have demonstrated constituent redistribution when irradiated or with thermal treatment. [1,2]**

- **Path Forward: Thermodynamic data is key to predicting the possibilities of effects such as constituent redistribution within the fuel rods and interaction with cladding materials.**

1. Y.S. Kim, G.L. Hofman, S.L. Hayes and Y.H. Sohn, J. Nucl. Matl. 327, 27 (2004).
2. Y.H. Sohn, M.A. Dayananda, G.L. Hofman, R.V. Strain and S.L. Hayes, J. Nucl. Matl. 279, 317 (2000).

Postirradiation optical metallography and measured constituent redistributions in T179 fuel at 1.9 at.% burnup. Taken from Kim et al. Note the U depletion and Zr enrichment in the center zone and U enrichment and Zr depletion in the intermediate zone. Energy Dispersive Spectroscopy (EDS) within an SEM was used to determine the concentration variations

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It is possible to experimentally benchmark thermodynamic information, i.e. heats of solution, directly from the binding energy shifts of core levels in metallic alloys.

Plot of experimental binding energy shifts (y axis) versus the predicted values derived from heats of solution (x axis). Note the high degree of correlation, with only a few outriders away from the y = x line.

**Y AXIS = ΔE_{exp} = $E_{alloy}(Z) - E_{pure}(Z)$**
These are elementally specific experimental core binding energies. A is the dopant or solute, with atomic number Z. B is the host material or solvent.

X AXIS = ΔE_{calc} = $E(Z,B) + E(Z+1, Z) - E(Z+1,B)$
These are heats of solution!
Taken from Steiner et al. [3]

- **We can benchmark heats of formation and study the kinetics using core level spectroscopy.**
- **Use small (low activity) actinide samples in the extant Fano Spectrometer in Rm 1226/B235 and LLNL Computing Facilities**
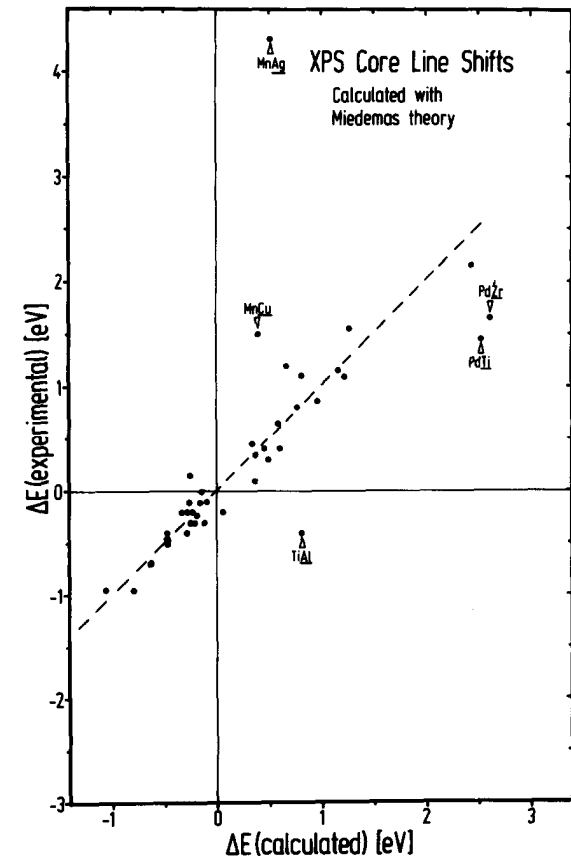
3. P. Steiner, S. Huefner, M. Martensson and B. Johansson, Solid State Communications 37, 73 (1981).

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Generality of Effect

Shown here is the earlier result of Jolly [4], demonstrating the empirical correlation of binding energy and thermodynamical energies.

While Martensson, Johansson, Steiner and Huefner [2,5] provided a powerful theoretical underpinning and the experimental correlation in metal alloys, ten years earlier Jolly et al reported the empirical correlation of spectroscopic and thermodynamic data for a wide range of materials and compounds, including oxygen and carbon containing materials. Thus, although the theoretical foundation is the most firm for the metal alloys, in part because of their strong screening of charges, there is ample evidence of the validity of the approach for a wide range of materials. This bodes well for the generality of the approach, including non-metallic systems, especially systems such as TRISO.

Thermochemical Estimates of XPS Shifts
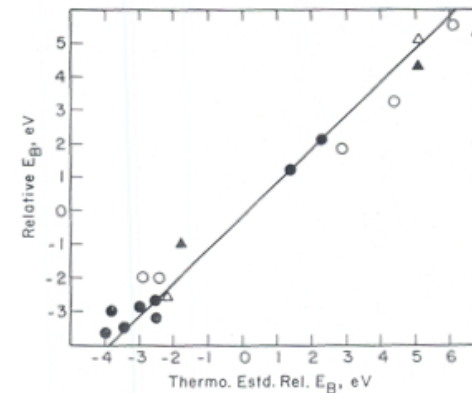
Plot of core binding energies for solid compounds vs. thermodynamically estimated energies. Solid circles correspond to nitrogen 1s binding energies; open circles correspond to carbon 1s binding energies; solid triangles correspond to iodine core binding energies; open triangles correspond to boron 1s binding energies.

4. W.L. Jolly, "The Estimation of Core-Electronic Binding Energy Shifts Using the Concept of the Equivalence of Equally Charged Cores," in "Electron Spectroscopy," ed. D.A. Shirley, 1970; W.L. Jolly and D.N. Hendrickson, J. Amer. Chem. Soc. 92:7, 1863(1970).
5. N. Martensson and B. Johansson, Solid State Comm. 32, 791 (1979).

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Core level shifts have been seen in Actinide Alloys. [6]
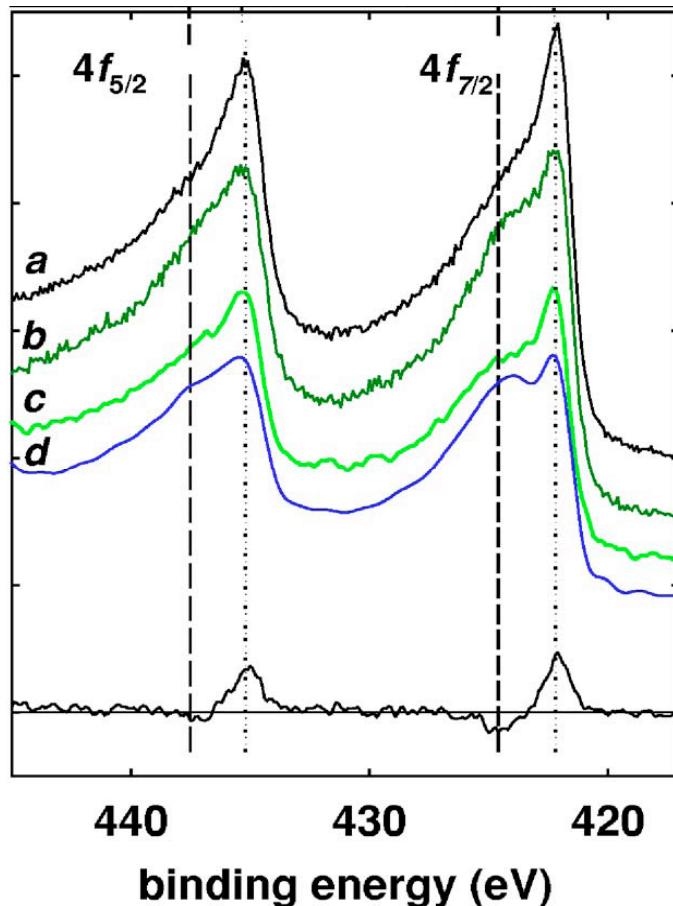
Core level shifts have been observed in actinide alloys. For example, the system Pu(1-x)Am((x) has been investigated by Baclet et al. [6]

Although the shifts are small, there is a shift between the alpha Pu and the alloy sample.

Pu 4f core level XPS data are presented here.
(a) alpha Pu like; (b) delta Pu like;
(c) Pu74%Am26%; (d) Pu64%Am36%
Taken from Baclet et al [6]

The situation shown here is a worst case: Pu is the host. Host effects are usually more difficult to observe than dopant effects as shown on the next viewgraph.

6.   N. Baclet, M. Dormeval, L. Havela, J. M. Fournier, C. Valot, F. Wastin, T. Gouder, E. Colineau, C. T. Walker, S. Bremier, C. Apostolidis, and G. H. Lander, PRB 75, 035101 (2007).

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We have had prior experience with these alloying measurements and analyses. [7]
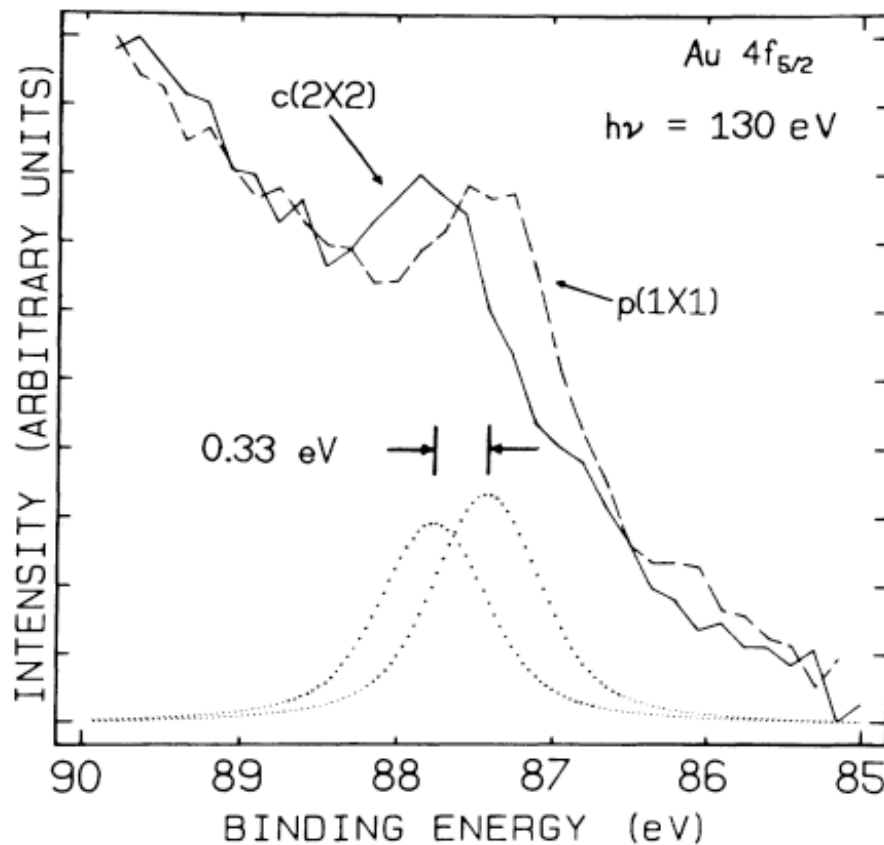
Here is an example of a dopant shift, involving surface alloying.

The Au p(1x1) is an overlayer, the Au c(2x2) is a surface alloy. Most of the sample is Cu, with only a little Au.

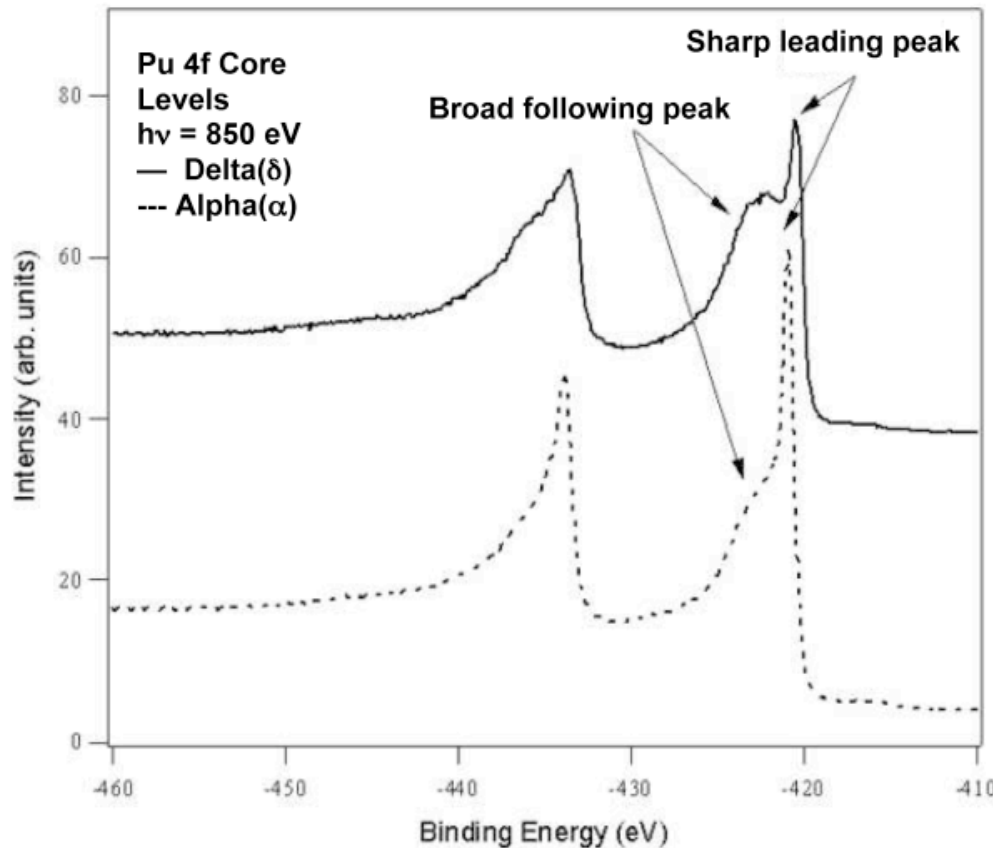These measurements were made by Tobin et al in 1987 and included an analysis with heats of solution.

Taken from Hansen et al. [7]

7.   J. C. Hansen, J. A. Benson, W. D. Clendening, M. T. McEllistrem, and J. G. Tobin, PRB 36, 6186 (1987).

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We have had prior experience with experimentation upon Pu. [8]

Shown here is the only synchrotron radiation generated spectrum of the Pu 4f levels. [8]

Core-level photoemission spectra from a large crystallite δ-Pu sample and a polycrystalline α-Pu sample are shown here. These spectra were collected with a photon energy of 850 eV and a bandpass of about 350 meV. Note that two large components are visible in each spectral structure, a sharp feature at low binding energy and a broad feature at higher binding energy. These data were taken at the Advanced Light Source in Berkeley, CA.
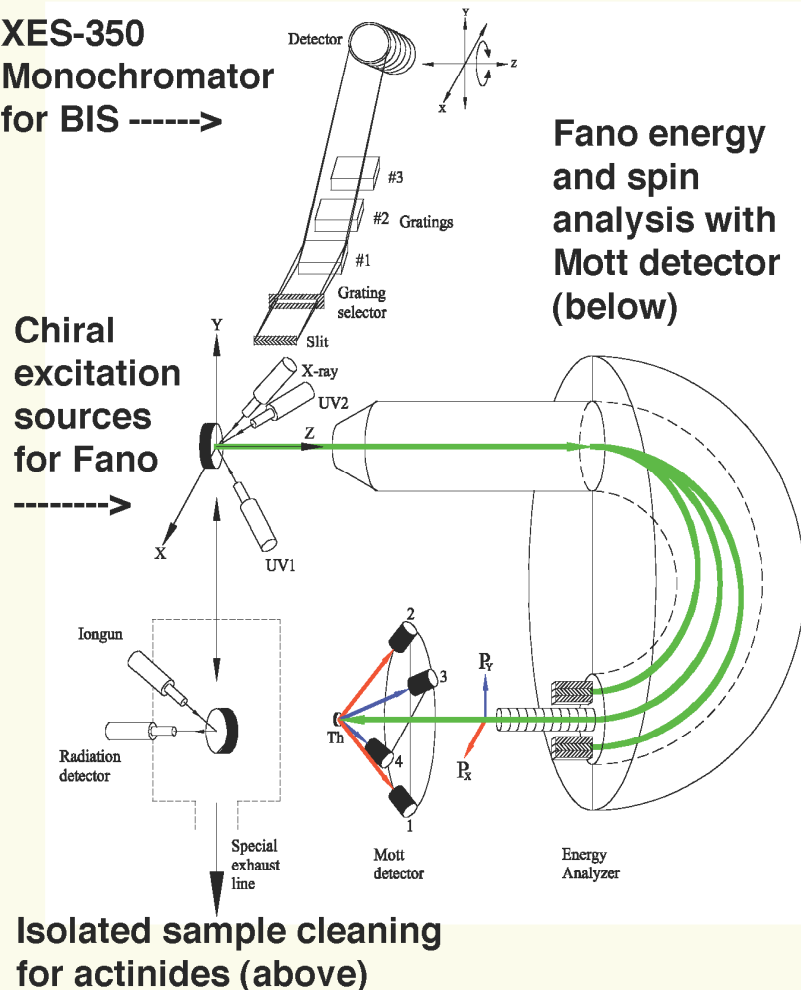
8.   J.G. Tobin, B.W. Chung, R. K. Schulze, J. Terry, J. D. Farr, D. K. Shuh, K. Heinzelman, E. Rotenberg, G.D. Waddill, and G. Van der Laan, Phys. Rev. B 68, 155109 (2003).

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XES-350 Monochromator for BIS ------>

Chiral excitation sources for Fano -------->

Fano energy and spin analysis with Mott detector (below)

Isolated sample cleaning for actinides (above)

The experiments will be performed in a spectrometer recently brought on line in Room 1226 in B235 at LLNL.

Here is a schematic describing the extant Fano/BIS Spectrometer.[9] (BIS stands for Bremstrahlung Isochromat Spectroscopy, or high energy Inverse Photoelectron Spectroscopy.) Initially, we will employ small (low activity) actinide samples for this project. Ultimately, the spectrometer will include specialized capabilities for handling Pu samples. For example, the long vertical manipulator will allow the isolation of the radioactive byproducts of sample preparation and cleaning from the analysis station yet also permit rapid access of the analysis position, so as to minimize surface corruption after cleaning. The spectrometer has already been used to produce publishable data. [9]

9.   S.-W. Yu and J.G. Tobin, Phys. Rev. B 77, 193409 (2008).

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Plan for Year One: FY09 - October 2008 through September 2009
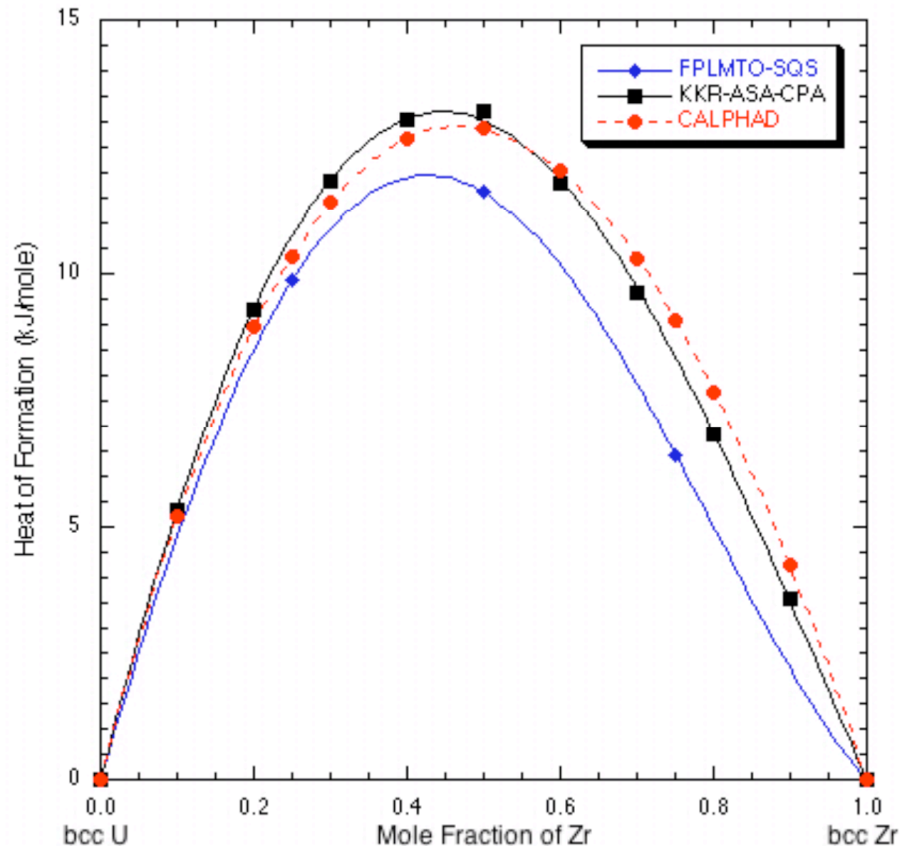
We will concentrate our efforts on the low activity system U(1-x)Zr(x) and experimentally benchmark the calculations by our collaborators at LLNL. [10]

Show here are the heats of formation (or solution) for the U(1-x)Zr(x) system, calculated by Turchi et al. [10]

10.   Patrice E. A. Turchi, Alexander I. Landa, Per A. Soderlind, Leventes Vitos and Andrei Ruban, "Ab initio and CALPHAD Approaches to Thermodynamics of U-Zr Alloys," NN3.3, Spring MRS Meeting, San Francisco, CA, USA, March 2008

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Science Impact:

Development of Novel, Environmentally Friendly Nuclear Fuels via Numerical Simulations and Projections, enabled by Experimental Benchmarking of Thermodynamic and Kinetic Properties of Advanced Nuclear Fuel Materials